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Microanalysis of Glass Fluid Storage Vials from The Invertebrate Zoology Collection at the National Museum of Natural History

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Glass alteration is the process by which modifier ions in a glass matrix undergo an ion exchange reaction with water in the surrounding atmosphere or environment.This process leads to the depletion of such ions from the bulk glass and the formation of a surface hydrated silicon-oxygen gel layer [1,2,3].There are a few common phenomena that can occur in significantly altered glass including increased opacity, microcracking or crizzling within the altered layer, and larger scale cracking and failure of the glass object itself [3,4].As glass alteration progresses over time, the process can begin to significantly degrade the appearance and structural integrity of the glass object. Cultural heritage institutions are one of the few environments in which glass is stored for long enough periods of time for the alteration of glass to be readily tracked, and in which it can become a significant challenge [4].

Typically, discussions of glass in cultural heritage institutions revolve around the objects in a collection that are comprised of glass themselves. However, in many natural history-focused collections, the glass is used tostore collections, particularly in fluid storage, and these vessels represent an overwhelming majority of glass in the collections as a whole. This is the case for the Smithsonian's National Museum of Natural History, which houses millions of specimens, stored in preserving fluid, and contained in glass jars or vials [5,6].The aqueous environment in which these glassesare kept accelerates and exacerbates the degradation of these containers through glass alteration.As this alteration progresses, the integrity of the glass containers becomes compromised, often leading to the fracturing and sometimes complete failure of the jar or vial. Broken jars or vials can result in the irreparable loss of the specimens, including type specimens, and also present a safety risk for those working in these collections [7].

Several glass vials were removed from fluid storage in the Invertebrate Zoology Collection at the Smithsonian's National Museum of Natural History. These vials were made available for analysis at the Museum Conservation Institute as a preliminary study of fluid storage glass. While there are no recorded dates associated with these vials, they span a wide range of manufacturing techniques from different historical periods [8]. Compositional analysis through X-ray florescence (XRF) showed the presence of several heavy metals such as antimony and arsenic which are also typically indicative of historic manufacturing techniques commonly used in the early 20th century [9].

Three of the vials, each with different observable features of alteration [Fig.1] were cross-sectionedand polished and analyzed usingscanning electron microscopy and energy dispersive X-ray spectrometry (SEM-EDS) using a Hitachi S3700N SEM and Bruker XFlash 6|60 X-ray detector. Bruker Esprit v2.1 was used in data processing and quantification of the glasses. Elemental mapping of the vial cross-sections made it possible to clearly visualize the altered regions as areas with significantly lower concentrations of sodium relative to the composition of the unaltered glass [Fig. 2]. The thickness of these regions were observed to differ from negligible (nm scale) to spanning the entire width of the vial wall (which differed for each vial and ranged from 1 mm to 2.5 mm). Additionally, the interface between the altered regions and bulk glass was observed to

be quite sharp when analyzed using a 5 kV electron beam. The sodium concentration profile across this interface (Figure 2b) was used to measure the width of the interface zone which was found to be approximately several hundred nanometers. The spatial resolution of the Na signal defined by 90% of the emitted X-rays is ≈240 nm and 200 nm for the altered and bulk glasses respectively, based on an electron scattering simulation to estimate these values [10]. Elemental mapping also allowed for the observation and identification of alteration driven precipitate formation inside some of the internal cracks within the altered vials.

Quantitative compositions were obtained from both the bulk and depleted regions, and in addition to lower sodium concentrations these measurements showed the sum of all masses were well below 100% in the altered zone. This low sum total is attributable to the significant presence of hydrogen in the altered region,which cannot be measured directly by SEM-EDS, and is consistent with this region representing a hydrated silicon-oxygen gel. The presence of hydroxyl groups was later confirmed by infrared spectrometry, namely microscope-based FTIR analysis ofthe altered and unaltered glass. Specifically, a prominent broad O-H stretch at ≈3500 cm^{-1} was observed in the spectrum obtained from the altered region, and was absent in the spectrum from the bulk glass.

The dramatic alteration observed in these vials, whichprior to extraction for analysis had been in active use to house specimens, points to the pressing need for larger studies of the glass used in the storage of natural history collections. Specifically, questions remain surrounding the exact rates at which glass jars and vials may alter and degrade in different aqueous preservation fluids. Ideally, further study would seek to determine what compositions of glass are more stable under these unique conditions, or if glass is indeed a suitable material for long term fluid storage of such museum collections in general.

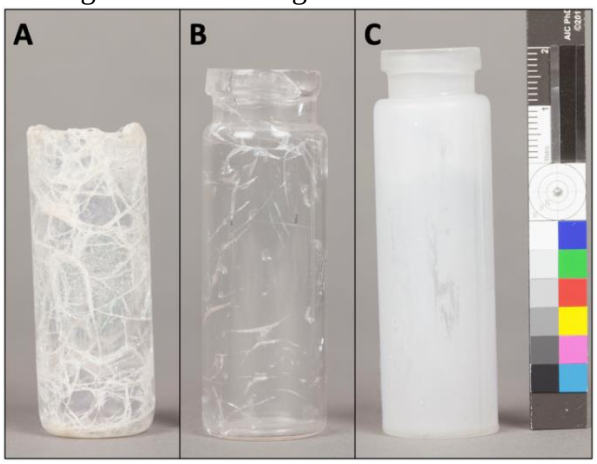

Figure 1. The three vials chosen for cross-sectioning and analysis. These vials represent a range of alteration responses from extensive cracking and vial failure (A) to larger scale cracking of otherwise clear glass (B), to increased opacity with no obvious fracturing (C). Image credit: Keats Webb, MCI.

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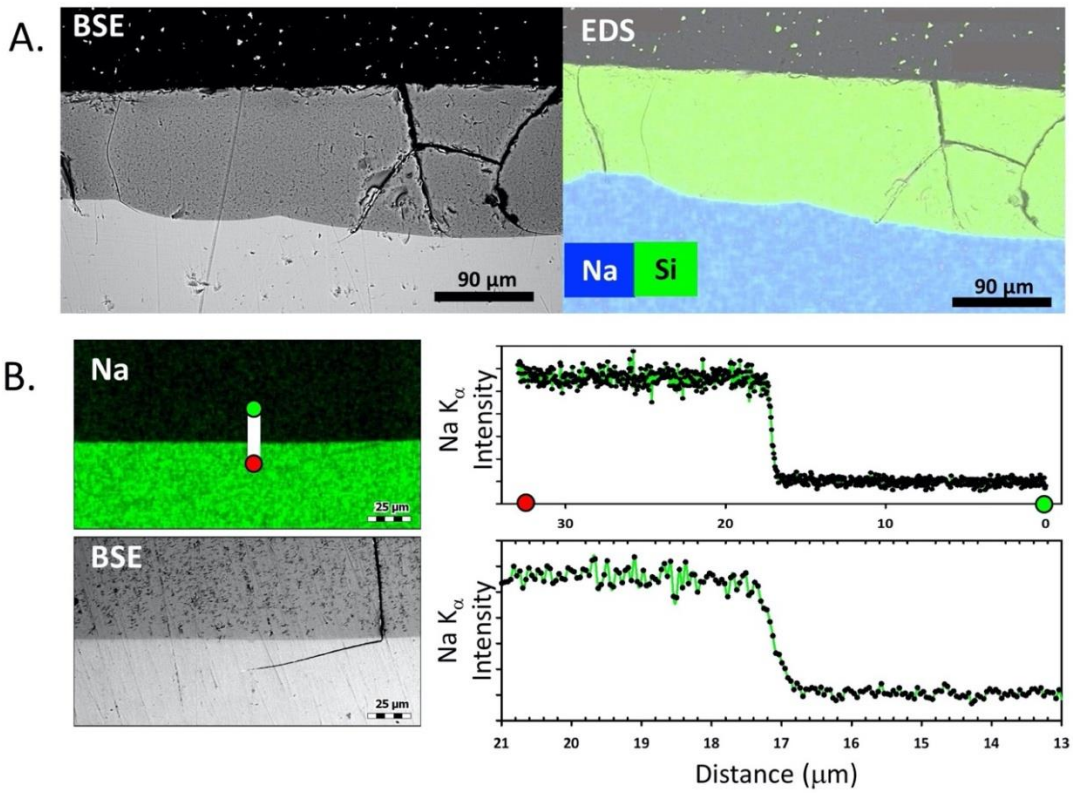

Figure 2. An example of a glass alteration zone in cross-section. A. These images were taken from the outer surface of the vial shown in Fig. 1a. The darker region in the backscattered electron (BSE) image (left) corresponds with a significant reduction in sodium and potassium concentrations as seen through EDS mapping of the region (right). B. BSE and corresponding sodium EDS images (left) of the interface between the glass alteration zone and the bulk glass. Na profile taken across this interface, averaged across a wide 1D line scan, seen at two length scales (right).

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